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<p>(54) Title: TOUGH, WEAR- AND ABRASION-RESISTANT, HIGH CHROMIUM HYPEREUTECTIC WHITE IRON</p> <p>(57) Abstract</p> <p>A tough, wear- and abrasion-resistant, high chromium, hypereutectic white iron alloy, with a composition by wt.% of >4.0 C, 25-45 Cr, 0-15 Mn, 0-10 Mo, 0-10 Ni, 0-2 B and 0-5 of at least one of Ti, W, Ta, V and Nb, subject to the proviso that Ti + W + Ta + V + Nb = 15 max., the balance, apart from incidental impurities, being Fe. The recommended super-heating range is 20-100°C above the liquidus for a particular composition, for pouring prior to casting to a minimum thickness of 10 mm. The microstructure is characterised by a volume fraction > 20% of primary, acicular, M₇C₃ - type carbides of mean cross-sectional dimension of 75µ max. in a eutectic matrix of eutectic and secondary carbides and austenite and/or martensite. The alloy in its softest condition, exhibiting stabilised austenite, substantially free of martensite, has a hardness of about 450 HV; in the as-cast state, the hardness typically ranges from 600-700 HV; after appropriate heat treatment, (e.g. heating at 900°C for 2-3 hours, followed by furnace or air cooling), the hardness range can be increased to 850-900 HV. The hardened alloy can be applied to such wear-and abrasion-resistant components as grizzly bars, hammer tips in hammer mills, sinter blow bars, coal and bone pulverisers, slurry spray nozzles and lining plates in chutes and crushers. The above components are typically assembled in the form of composites, with a copper liner at the interface, either by vacuum brazing pre-cast alloy on to, or casting in situ on or around, a strong and tough metallic substrate.</p>		

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TOUGH, WEAR- AND ABRASION-RESISTANT, HIGH CHROMIUM HYPEREUTECTIC WHITE IRON

This invention relates to improved wear or abrasion resistant high chromium white cast irons, and to a method of producing such irons.

BACKGROUND OF THE INVENTION

In a paper "Abrasion Resistance and Fracture Toughness of White Cast Irons", Metals Technology, November 1979, 412-419, I.W. Sare details the performance of a range of alloy white cast irons in abrasion resistance and fracture toughness tests.

10 The alloys principally were of hypoeutectic composition, but included two alloys of hypereutectic composition having inter alia 4.42%C with 33.2% Cr and 5.24% C with 35.5% Cr, respectively. Specimens, with one exception, were sand cast to provide plates of 5 mm and 12 mm thickness, although none of the latter were of hypereutectic composition. The one exception to such sand casting was a chilled casting of the 35% Cr alloy.

Sare indicates that the hypereutectic alloy has a composition comparable to many commonly used hardfacing alloys. Examples of proposals relevant to hardfacing are set out in
20 U.S. patents 2,024,992 and 2,355,271, French patent 906,354, West German patent 1,908,853 and Russian patents 312,708, 321,335 and 411,974. Hardfacing has the benefit of making wear resistant an article onto which weld metal of a wear resistant composition is deposited. However, hardfacing is subject to well documented disadvantages including thickness limitations, low deposition rates, distortion, high labour costs, composition variation due to dilution by substrate metal, spalling due to relief checking, high consumable costs, composition
30 limitations, alloying element loss and constraints on heat treatment.



The Sare paper indicates that a hypereutectic white cast iron, in the as cast condition, has a surprisingly good combination of abrasion resistance and toughness. This result is said to be in stark contrast to the widely held view that hypereutectic cast irons are extremely brittle and even less abrasion resistant than hypoeutectic compositions. Such views are indicated as denying the very successful application of white cast irons as weld-deposited hardfacing alloys. However, the disparity between that result of Sare and the widely held view of others has been found to exist in the extremely limited thickness of the specimens used by Sare, 5 mm for the hypereutectic alloy, which is slight and only comparable with hardfacing deposit depths. That is, when one seeks to produce a hypereutectic casting of wall thickness significantly exceeding 5 mm, it is found that the casting has poor toughness and is liable to crack in the mould. This experience also is completely in accord with hardfacing experience, but the brittleness of hypereutectic white cast iron hardfacing normally is mitigated to a degree by the toughness of the material on which it is weld-deposited.

The prior art in relation to the use of white cast irons other than by hardfacing is extensive and principally is concerned with the manufacture of complete articles such as balls for grinding mills, pump components such as pump housings, rolls for mills, liners for ball mill drums, and nozzles for spraying slurries. This is exemplified by U.S. patents 2,268,426, 2,662,011, 3,410,682, 3,834,950, 3,849,078, 3,849,122, 3,941,589, 3,961,994, 4,043,842 and 4,382,828 and U.K. patent 1,119,516; while the above-mentioned U.S. patent 2,355,271 also has some relevance in this regard.



As is apparent from the prior art listed in the immediately preceding paragraph, the abrasion resistance of chromium white irons is a function of composition and of the microstructure obtained, as pointed out by the Sare paper. U.S. 3,410,682 correctly points out that a balance between abrasion resistance and toughness is difficult to achieve, and if a material displays superior abrasion resistance, it may be so brittle as to chip and spall under severe impact. U.S. patent 3,834,950 recognises the need, in achieving superior abrasion resistance, to have a microstructure characterized by primary carbides, rather than Fe_3C ; while U.S. patent 3,961,994 points to the need for as high a volume percentage of primary carbides as possible.

While U.S. 3,961,994 deals with a hypoeutectic composition, it proposes recourse to a high temperature forming from cast material and forging rather than reliance simply on casting, with or without heat treatment. In contrast, U.S. 3,834,950 relates to a cast alloy covering both hypo- and hyper-eutectic compositions, but subject to a severely constraining relationship between carbon and chromium content. Indeed, while 3,834,950 is based on an appreciation of the hardness of M_7C_3 carbides, that relationship is adopted to avoid those carbides. That is, 3,834,950 is directed to achieving primary carbides mainly of the face-centered cubic M_{23}C_6 type since, notwithstanding their inherent lower hardness compared with M_7C_3 carbides, this is recognised as preferable to the brittleness resulting from higher levels of M_7C_3 carbides achieved with higher carbon contents.

Thus, while some of the patent literature detailed above proposes the use of hypereutectic white irons, this



principally is in relation to hardfacing alloys. The casting of such irons conventionally is avoided in foundry practice, due to the formation of coarsely acicular M_7C_3 primary carbides which can cause extensive cracking of a casting in the mould or premature brittle failure under repeated impact loading conditions in service. This problem is alluded to in U.S. 2,268,426, covering both hypo- and hyper-eutectic cast alloy, wherein it is indicated that the alloy may be employed in the construction of any device which may be cast into the desired shape and in which the device is not subjected to a great amount of shock or impact which may lead to fracture. Moreover, U.S. patent 2,662,011 indicates that with the exception of intricate shapes necessitating sand casting, the hypoeutectic alloys it proposes can be chill cast to improve properties. However, despite this disclosure, U.S. 2,662,011 teaches the avoidance of higher carbon contents, i.e. those necessary for a hyper-eutectic white iron, since such contents cause a decrease in hardness and undesirable carbide needles. Furthermore, U.S. patent 4,382,828 proposes casting its hypoeutectic white irons in a permanent metal mould, but removal of the solidified casting from the mould at a temperature above the A_{C3} (alpha-gamma conversion temperature), and cooling the casting sufficiently quickly to prevent formation of pearlite and secondary carbide precipitation. However, even with the hypoeutectic compositions of U.S. 4,382,828, the rate of cooling has limits due inter alia to stress build-up and danger of cracks and, short of modifying the composition, cooling can need to be less than required to prevent pearlite formation and secondary carbide precipitation. U.S. 4,382,828 does not explicitly detail the expected consequences of moving into the



higher carbon contents providing hypereutectic white irons, although these are implicit in those limits and the criteria underlying its proposal are relevant to hypo-, rather than hyper-, eutectic white irons.

SUMMARY OF THE INVENTION

The present invention has as its object the provision of an improved hypereutectic white cast iron having a high abrasion resistance combined with high fracture toughness.

As with the paper by Sare, and much of the foregoing patent literature, the invention is based on a recognition of the abrasion resistance of white cast irons and, in the case of hypereutectic compositions, the importance of M_7C_3 carbides in achieving this. In common with the Sare reference, the invention also is based on an appreciation of the importance of both the volume fraction of those carbides in relation to abrasion resistance and their particle size in relation to fracture toughness. However, the invention additionally is based on a recognition of the need to be able to achieve a substantially constant microstructure substantially throughout a casting significantly in excess of 5 mm thickness in order to meet the requirements for the majority of applications for which a tough, abrasion resistance material is required.

According to the invention, there is provided a tough, abrasion resistant ferrous alloy comprising a cast hypereutectic white iron having in excess of 4.0 wt.% carbon, from 25 to 45 wt.% chromium and, apart from additions hereinafter specified, the balance being iron with incidental impurities, such as up to 2 wt.% silicon; the alloy as cast having a minimum thickness dimension of at least 10 mm, and a microstructure comprising a volume fraction in excess of 20% primary carbides of acicular



M_7C_3 type and a matrix of eutectic composition; the primary carbides of the M_7C_3 type substantially throughout the alloy having a mean cross-sectional dimension of not more than 75μ . The matrix comprises eutectic carbide plus austenite, martensite or a mixture of austenite and martensite.

The alloy according to the invention may have from 4.0 to 7.5 wt.% carbon; the preferred carbon content being from 4.5 wt.% to 5.5 wt.%. However, as detailed hereinafter, the carbon content may be of an extreme level up to 9 wt.% under certain conditions. The chromium content preferably is in excess of 30 wt.%, such as from 30 to 40 wt.%. 10

The alloy of the invention may include alloying additions. These include manganese up to 15 wt.%, nickel up to 10 wt.%, molybdenum up to 10 wt.%, boron up to 2 wt.%, and up to 5 wt.% each of at least one of titanium, tungsten, vanadium, tantalum and niobium. Except with at least 5 wt.% manganese, there preferably should be a total of not more than 15 wt.% of elements comprising titanium, tungsten, vanadium, tantalum and niobium. However, with not more than 5 wt.% molybdenum, that total preferably does not exceed 10 wt.%. Additionally, boron preferably is present in not more than 1 wt.% in the absence of at least 5 wt.% manganese, to avoid resultant cracking of the alloy. In the presence of 5 to 15 wt.%, preferably 10 to 15 wt.% manganese, the boron content can be increased up to 2 wt.% without cracking. When manganese and nickel are present, this preferably is at a level in excess of 2 wt.%, most preferably in excess of 4 wt.%. 20

In most cases, the eutectic composition matrix of the as cast alloy without significant alloy additions is characterized by a mixture of austenite and martensite plus 30



secondary carbides. The matrix may in such cases have from 40 to 60% of one of austenite and martensite relative to the other in the absence of a sufficient quantity of strong carbide forming elements. However, the formation of martensite in the as cast alloy matrix can be substantially fully suppressed by inclusion of an austenite stabilizer such as at least 4 wt.% manganese, nickel or a mixture of these. Electron microprobe analysis shows that manganese is substantially uniformly dispersed in the primary and secondary carbides and in the retained austenite of the matrix. Thus, the addition of manganese increases the volume fraction of primary carbides and results in toughening of the matrix and providing the capacity for work hardening of the matrix in service as with Hadfield steels. Nickel also stabilizes the matrix austenite and additionally increases corrosion resistance, for example in retarding high temperature oxidation.

The elements molybdenum, boron, titanium, tungsten, vanadium, tantalum and niobium, due to their strong carbide forming action, effectively increase the microhardness and volume fraction of primary carbides. The final composition of the alloy containing these elements is dependent upon the atomic weight of the elements, the limits of their solubility in the M_7C_3 primary carbides and in the retained austenite. To the extent that these elements or their carbides are soluble in the M_7C_3 primary carbides, they increase the volume fraction and microhardness of the latter. However, to the extent that they are added in excess of such solubilities in the matrix and primary carbides, they themselves provide additional primary carbides which, while of various types other than M_7C_3 carbides, have extreme microhardness and enhance wear resistance due both



to their hardness and the increased overall primary carbide volume fraction.

For a given carbon and chromium content which were, if not for the carbide forming elements molybdenum, boron, titanium, tungsten, vanadium, tantalum or niobium, would enable a substantial or partially austenitic matrix, such austenitic matrix can be achieved by at least 4 wt.% manganese, nickel or a mixture of this. However, an alternative or additional means for achieving such austenitic matrix is to increase the carbon content of the alloy, such as by about 1 wt.%, to offset depletion of carbon by the carbide forming elements which tends to provide a martensitic rather than austenitic matrix.

The extent of solubility of each of titanium, vanadium, tungsten, tantalum and niobium in the alloy effectively is from 0.5 to 2 wt.%. The extent of solubility of molybdenum in the alloy is effectively 8 wt.%. To the extent that they are dissolved in the matrix, they can be precipitated as secondary carbides, thereby providing some hardening of the matrix and increase in abrasion wear resistance. Each of those elements most preferably are present at from 1.0 to 5.0 wt.%, subject to the above-mentioned overall constraints, so as to additionally provide primary carbides enhancing abrasion resistance. These elements plus boron, due to the strong carbide forming action they exhibit, enable use of alloys having increase carbon contents up to a limit of about 9 wt.% carbon.

The upper limits for titanium, tungsten, tantalum, vanadium and niobium are set in part by their effect in increasing the liquidus temperature of the alloy, and in decreasing fluidity of the alloy melt. The latter effect is found to be offset to a sufficient extent by a sufficient



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addition of manganese, which preferably is in excess of 5 wt.% where those carbide forming elements total more than 10 wt.%.

The above-discussed carbide forming elements can be added in any convenient form. Most conveniently, they are added as alloys such as ferro-alloys. In addition to the benefits already discussed, it is found that particularly where they are present in an amount exceeding about 1.0 wt.%, they provide nucleating sites for the M_7C_3 primary carbides to an extent resulting in grain refinement of the M_7C_3 carbides.

10 In the absence of austenite stabilizing and strong carbide forming elements, the M_7C_3 primary carbides typically are present in a volume fraction in excess of 30% to about 60%. The austenite stabilizing elements, due to their solubility in the M_7C_3 carbides can increase the volume fraction of those carbides to in excess of 40% to about 75%. The strong carbide forming elements are extremely variable in their effect on the volume fraction of M_7C_3 carbides. The effect of boron, despite its quite small levels of addition, is more pronounced than that of the other carbide forming elements. However, the carbide
20 forming elements normally are used to increase the volume fraction of M_7C_3 carbides to an upper limit of about 80%, with the lower limit being in excess of from 30 to 55%, depending on which of the carbide forming elements are used, whether they are used in combination and whether they are used in conjunction with one or more austenite stabilizing elements. The carbide forming elements additionally can contribute respective primary carbides; although these generally should be limited to increasing the total volume fraction of by not more than about 10 to 20% at the lower end of the M_7C_3 range and, at the upper
30 end of that range, so as not to increase the total primary



carbide content to above about 80 to 85%.

The principal influences of the carbide forming elements is in the increased abrasion resistance resulting from their primary carbides (and their secondary carbides after heat treatment), their refinement of the grain size of the M_7C_3 carbides and increasing the volume fraction of the latter carbides. In relation to the first two of these influences, it is found that similar effects can be achieved by adding these elements as their carbides in fine particulate form rather than as a respective metallic form. Where the elements are added as their carbides, the quantity of each element preferably is the same as for their addition in metallic form. However, where the elements are added as their carbides, the carbon content of the remainder of the alloy preferably does not exceed 7.5 wt.%, and most preferably is from 4.0 to 5.5 wt.%, such as from 4.5 to 5.5 wt.%.

Where such fine particulate carbides are added, they may at least partially remain in suspension rather than go fully into solution in the melt. This is particularly likely where the degree of superheating of the melt is limited as hereinafter proposed. Care therefore is required to ensure that the particulate carbides are substantially uniformly dispersed at the time of pouring the melt. Molybdenum carbide is likely to be fully dissolved in the melt, even with such limited superheating, and less care therefore is required where only that carbide is used. Similarly, where carbide forming element is added in metallic form, the resultant carbide may at least in part come out of solution and, in such case, care is required to ensure that it is substantially uniformly dispersed at the time of pouring. Also in such case, it is desirable that the period for



which the melt is held prior to pouring is kept to a minimum so as to avoid excessive growth of the carbide particles.

In one important aspect, the alloy of the invention is achieved by casting it against a work surface of a substrate component to be protected against abrasion, so as to achieve a metallurgical bond between the cast alloy and the component.

The component preferably is one which provides increased toughness and impact resistance in the composite article comprising the substrate and alloy; while the substrate also

10 most preferably has good machinability and weldability.

Suitable materials for the substrate include ductile steels such as mild steel, as well as alloy hardened steels and suitable cast steels and irons.

Where the alloy of the invention is cast against a substrate to provide a composite article, the required metallurgical bond preferably is achieved by diffusion, preferably facilitated by a filler metal provided over the work surface of the substrate. The filler metal is to be one which melts, on casting of the alloy, and which most preferably wets the

20 substrate surface and, by diffusion, migrates into the surface of the substrate and into the cast alloy immediately adjacent thereto. Copper is the preferred filler metal and may be provided over the surface of the substrate either by deposition or as thin sheet material. The resultant metallurgical bond between the substrate and cast alloy is found to have a shear strength in excess of 300 MPa (about 20 tons per square inch).

The composite article enables the alloy of the invention to be provided on a substrate readily able to be positioned and secured by any convenient means, if necessary
30 after machining and/or drilling of the substrate. However, in a



useful variant of such composite article the alloy of the invention can be cast so as to enclose a substrate, such as in providing a facing on all four side faces of a mild steel bar of square section for use as an abrasion resistant member of an ore feed chute, a hammer bar for a coal pulverizer, or the like.

In a variant of the above-described composite product, in which the alloy of the invention is cast in situ, the alloy may be pre-cast. In such case, the second component then is applied to a work area of the substrate component to be
10 protected, and secured to that area by brazing, such as vacuum brazing, to achieve a metallurgical bond between the alloy and substrate. A strong metallurgical bond in excess of 300 MPa is achieved, particularly if brazing is at a temperature sufficient to cause diffusion between the alloy and substrate. The brazing may be performed in the presence of a filler metal, as discussed above, such as in the manner disclosed in U.S. patent 3,355,264. Copper again is the preferred filler metal, and the brazing temperature preferably is such that the filler metal diffuses into both the substrate and pre-cast alloy.

20 The hypereutectic alloy of the invention is found to provide extreme abrasion resistance due to its volume fraction of at least 20% of M_7C_3 primary carbides and, where present, other primary carbides. The alloy also has good fracture toughness, and this is significantly enhanced where the alloy is cast in situ against, or is brazed to, a suitable substrate. In the as cast condition, the alloy having a matrix characterized by stabilized austenite substantially free of martensite has a hardness of about 450 HV. However, with heat treatment, that
30 hardness can be increased to about 850 HV, but with the manganese present for fully retained austenite necessitating a



longer heat treatment soak at elevated temperatures than otherwise required. With about equal proportions of austenite and martensite present in the matrix, the as cast hardness typically is about 600 to 700 HV but, with heat treatment, this can be increased to about 900 HV. These hardness values are for alloys substantially free of primary carbides of carbide forming alloy elements other than chromium; although these significantly increase overall hardness above those values due to their own inherent hardness, and also their effect in refining the grain size of the M_7C_3 primary carbides and increasing the volume fraction of the latter. In each case, the presence of up to 2 wt.% boron or 5 to 10 wt.% of other carbide forming elements increases the as cast hardness by about 100 to 300 HV units.

Age hardening of the alloy of the invention may be by soaking at from 750 to 1000°C, for example 2 to 3 hours at 900°C, followed by furnace or air cooling. The heat treatment preferably does not exceed 1000°C. However, the heat treatment may follow on from vacuum brazing pre-cast alloy to a substrate. In such case, the heat treatment initially may include heating the alloy and substrate above the melting point of copper (1083°C), such as at 1100°C, for a time sufficient for the brazing operation, followed by soaking at a temperature below 1000°C such as at 900°C.

Having broadly outlined the present invention, it is necessary to consider aspects of the invention relevant to the widely held view pointed out in the Sare paper as to hypereutectic cast irons being extremely brittle. As detailed above, the alloy of the invention is not extremely brittle, but rather it is characterized by good fracture toughness, particularly for an abrasion resistant material.



As will be appreciated, the liquidus and solidus lines for hypereutectic white irons diverge sharply with increasing carbon content. This divergence increases with most alloy additions, while the volume fraction of M_7C_3 primary carbides also increases with carbon and chromium content and, to a lesser degree, with alloy additions. These primary carbides develop as a nucleation and growth process during solidification of the melt in the temperature interval between the liquidus and solidus temperatures. A consequence of this latter factor is that a coarse, acicular carbide structure, typical of experience with brittle hypereutectic cast irons, can develop. However, we have found that the problems presented by such structure can be avoided by control over a number of factors.

A first factor relevant to achieving the alloy of the invention is the degree of superheating on pouring of the melt from which the alloy is cast and for optimum control it is highly desirable that the liquidus temperature for a given alloy composition be ascertained. For a sand mould cast alloy not including a significant quantity of M_7C_3 primary carbide grain refining alloy elements, it is undesirable that the melt be poured at more than 40°C above the liquidus temperature if cracking of the casting or low fracture toughness is to be avoided due to excessive growth of primary carbides. The melt can be poured at a temperature of more than 40°C above the liquidus temperature, up to a limit of about 100°C , provided that the rate of cooling of the melt to the solidus is greater than 50°C per minute, and preferably greater than 100°C per minute. The need for such increase in cooling rate again is to refine the primary M_7C_3 carbide size to avoid cracking of the casting or low fracture toughness. Similarly, due to the effect



of the alloying additions, when added in metallic form in the case of carbide forming elements, in refining the primary carbide grain size, their use can enable the melt to be poured at a temperature of up to 100°C above the liquidus temperature. However, it is preferred not to rely on such alloy additions alone when the melt is poured at a temperature more than 40°C above the liquidus; it still being desirable for fracture toughness to cool the melt through to the solidus temperature at a cooling rate of at least 50°C per minute, and most preferably at least 100°C per minute. Preferably the melt is poured at a temperature not more than 20°C above the liquidus temperature, and most preferably as close as possible to the liquidus such as not more than 5°C above the liquidus.

The alloy of the invention is characterized by a minimum thickness dimension of at least 10 mm, and a volume fraction of M_7C_3 primary carbides in excess of 20% with those carbides having a cross-sectional dimension of not more than 75 μ . Such characteristics are achieved by the conditions of the preceding paragraph. In suitable compliance with those requirements, there are a number of alternatives available.

The above-mentioned cooling rates readily can be achieved, in the case of pre-cast alloy, by utilizing a sand or like mould and incorporating in the mould prior to casting a ferrous insert to be in direct contact with the alloy. In such case, the insert preferably is of a tough material, and most preferably is coated with a filler metal such as copper to achieve a metallurgical bond between the insert and alloy. For alloy castings having a minimum thickness dimension in excess of 30 mm, the insert preferably comprises at least about 10% by weight of the resultant product. For alloy pre-cast to

substantially greater dimensions, such as up to 70 mm, it is preferable to utilize a chill mould plus such insert in order to achieve the required cooling rate of not less than 50°C per minute, and preferably at least 100°C per minute. Alloy pre-cast to less than about 30 mm minimum dimension does not necessitate an insert and may suitably be cast in a zircon/chromite sand mould, but preferably is cast in a chill mould to achieve such required cooling rate.

10 For in situ cast alloy, the substrate can at least in part serve to achieve the required cooling rate, particularly where the substrate comprises at least about 10% by weight of the resultant composite article. However, for alloy cast to a minimum dimension of about 30 mm, it additionally is preferred to utilize a chill mould and/or an insert cast in the alloy.

For both pre-cast and in situ cast alloy the weight of the chill mould, the insert, substrate or combination of these preferably is such as to achieve a rate of cooling of at least 50°C per minute, most preferably at least 100°C per minute.

20 With recourse to the above casting conditions, including the degree of superheating of the melt when poured, it is found that the alloy is tough and has primary M_7C_3 carbides having a mean cross-sectional dimension not exceeding 75 μ . If that dimension of the carbides exceeds 75 μ , the alloy is prone to cracking and exhibits lowered fracture toughness. However, the casting conditions preferably are such that the mean cross-sectional dimension of the primary M_7C_3 carbides does not exceed 60 μ , and most preferably is less than 50 μ . These values can readily be achieved substantially throughout alloy cast to thickness of up to and exceeding 50 mm, by control over the melt
30 temperature when poured, the rate of cooling and/or alloy element

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refinement of those carbides. Moreover, it is found that even with primary carbides up to 75μ in mean cross-sectional dimension, stress build-up in the alloy does not occur to a level likely to give rise to cracking, or premature failure in service by spalling.

Most conveniently, the required constraints on casting of the alloy are more rigidly adhered to with increasing carbon and chromium content and, to a lesser extent, increasing alloy element content. However, it is found that despite the increasing volume fraction of M_7C_3 and other primary carbides with these increases, the alloy still enables production of crack-free castings with good fracture toughness. However, for a volume fraction of M_7C_3 carbides in excess of about 55%, it is preferable that their grains be refined by addition of the strong carbide forming elements and by a cooling rate down to the solidus in excess of 100°C per minute. These combined effects are particularly desirable where the mean cross-sectional dimensions of the primary carbides is not to exceed 50μ or even 60μ .

In the following tables I to IV, the volume fraction of primary carbides, and the measured liquidus and solidus temperatures for the range of alloys are set out.

Table I illustrates the influence of carbon content alone on the volume fraction of primary M_7C_3 carbides for Fe-35 Cr-carbon hypereutectic alloys, while Table II shows similar detail for chromium content for Fe-4.5 C-chromium alloys. Table III shows the influence of carbide formers tungsten, boron, titanium, vanadium and molybdenum on Fe-4.5 C-35 Cr hypereutectic alloys; the influence of niobium and tantalum being comparable to titanium. As will be evident,

total carbon exceeds 4.5% in each of alloys 3B to 3F; while it also should be noted that the volume fractions shown are those of M_7C_3 carbides only. Table IV illustrates the influence of manganese on the volume fraction of primary M_7C_3 carbides for Fe-4.5 C-35 Cr-Mn alloys.



TABLE I

ALLOY	PRIMARY CARBIDES VOLUME %	TEMPERATURE °C	
		LIQUIDUS	SOLIDUS
1A Fe-35Cr-4.5C	32	1386	1273
1B Fe-35Cr-5.0C	36	1401	1266
1C Fe-35Cr-5.5C	50	1482	1260
1D Fe-35Cr-6.0C	55	1495	1255

TABLE II

ALLOY	PRIMARY CARBIDES VOLUME %	TEMPERATURE °C	
		LIQUIDUS	SOLIDUS
2A Fe-4.5C-25Cr	27	1343	1235
2B Fe-4.5C-30Cr	30	1372	1262
2C Fe-4.5C-35Cr	32	1386	1273
2D Fe-4.5C-40Cr	34	1434	1278
2E Fe-4.5C-45Cr	36	1450	1285

TABLE III

ALLOY	PRIMARY CARBIDES VOLUME %	TEMPERATURE °C	
		LIQUIDUS	SOLIDUS
3A Fe-35Cr-4.5C	32	1386	1273
3B Fe-35Cr-4.5C-4WC	33	1393	1262
3C Fe-35Cr-4.5C-1B ₄ C ₃	51	1404	1225
3D Fe-35Cr-4.5C-2.5TiC	35	1410	1267
3E Fe-35Cr-4.5C-5V ₄ C ₃	40	1473	1261
3F Fe-35Cr-4.5C-4.5Mo ₂ C	34	1419	1242

TABLE IV

ALLOY	PRIMARY CARBIDES VOLUME %	TEMPERATURE °C	
		LIQUIDUS	SOLIDUS
4A Fe-35Cr-4.5C	32	1386	1273
4B Fe-35Cr-4.5C-2Mn	33	1390	1267
4C Fe-35Cr-4.5C-4Mn	34	1412	1262
4D Fe-35Cr-4.5C-6Mn	36	1406	1263
4E Fe-35Cr-4.5C-8Mn	38	1425	1253

To illustrate the invention, coal pulverizer peg wear components having dimensions of 115 x 70 x 25 mm were cast from alloy 1B (Table I). The components were cast in sand or shell moulds at a pouring temperature of 1420°C. They were found to be crack-free and to be characterized by a substantially uniform microstructure throughout, apart from a thin skin of less than 0.5 mm formed against the mould. The microstructure comprised a volume fraction of about 36% M_7C_3 primary carbides in a matrix of eutectic composition substantially free of martensite.

10 The wear components were vacuum brazed onto steel supports, to provide the required pegs, after a layer of 0.05 mm thick copper had been deposited on the supports. The brazing was effected at a temperature in excess of 1083°C and was found to provide a bond between the component and support in excess of 300 MPa. In use as moving pegs on a Riley coal pulverizer, the composite peg was found to have excellent abrasion resistance, giving a wear life in excess of 4 times that obtained with Ni-hard pegs, and to have a fracture toughness in excess of requirements for this application.

20 Further examples of the invention are set out in the following.

EXAMPLE I

A hammer mill, hammer tip wear components having the dimensions 100 x 75 x 25 mm were in zircon bearing shell moulds, at a pouring temperature of 1420°C. The alloy and resultant castings had the following characteristics:



Composition - chromium	31.8%
carbon	4.8%
manganese	3.9%
molybdenum	1.4%

Solidification temperature range: 1420°C - 1260°C

Microstructure primary M_7C_3 carbide

volume fraction	34%
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mean diameter	40 microns
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Matrix hardness - as cast	650 HV
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heat treated	840 HV
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Abrasion wear resistance	36.3 mgm
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Fracture toughness (K_{IC})	27.1 $MNm^{-3/2}$
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Bend tensile strength	850 MPa
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As in the following Examples II to VII, the wear resistance was determined by the high stress abrasion wear resistance test using a 6.8 kg loaded pin of 6.35 mm diameter, with 80 μ alumina as detailed by Diesburg et al., "Optimising Abrasion Resistance and Toughness in Steels and Irons for the Mining Industry" AMAX Symposium, Vail, Colorado 1974. Also as in Examples II to VII, the fracture toughness was determined with the procedure set out by Outwater et al., "Double Torsion Technique as a Universal Fracture Toughness Test Method", Fracture Toughness and Slow-Stable Cracking, ASTM STP 559, American Society for Testing and Materials, 1974, pp. 127-138.

The castings were found to be crack-free, and to be characterized by a substantially uniform microstructure throughout apart from a superchilled zone about 0.5 mm thick formed against the mould.

The wear components were vacuum brazed onto steel backing plates, after placing 0.05 mm thick copper shim



therebetween. The brazing was effected at a temperature in excess of 1083°C , and was found to provide a metallurgical bond with a shear strength in excess of 300 MPa. The resultant hammer tips then were heat treated by ageing at 900°C for 2 hours, followed by furnace cooling to ambient temperature.

In service in sugar cane shredder mills, the wear resistant component of the hammer tips were found to have excellent abrasion wear resistance, yielding a wear life in excess of 4-times that obtained with Ni-Hard castings and abrasion resistant hard facing deposits. In addition, the fracture toughness of the wear components was found to be in excess of requirements for this application; while that toughness, supplemented by the backing plates, enabled failure under extreme impact loading, such as due to tramp iron in the feed to the mills, to be avoided.

EXAMPLE II

Sinter blow bar wear components, having dimensions 230 x 50 x 35 mm were cast from an alloy having the following composition, and giving rise to the following characteristics:

Composition - chromium	31.5%
carbon	5.55%
manganese	0.5%
Solidification temperature range: $1480^{\circ}\text{C} - 1260^{\circ}\text{C}$	
Microstructure: primary M_7C_3 carbides	
volume fraction	53%
mean diameter	40 microns
Matrix hardness - as cast	690 HV~
heat treated	890 HV
Abrasion wear resistance	27.0 mgm
Fracture toughness (K_{IC})	$25 \text{ MNm}^{-3/2}$
Bend tensile strength	650 MPa

The alloy was cast in a zircon bearing shell moulds after positioning centrally in each mould a copper coated, 13 mm diameter x 230 mm long mild steel rod insert. The castings were found to be crack-free, and partial diffusion through the copper on sectioning of a component in the as cast condition. The components were heated above 1083°C in a normal atmosphere furnace to develop a full metallurgical bond between the cast alloy and insert. Final ageing at 900°C for 2 hours, followed by air cooling, increased the hardness of the castings to 890 HV.

10 In service, the blow bars exhibited a wear resistance ten times greater than Hadfield steel. Their fracture toughness properties were greater than the requirements for this application.

The blow bars of this Example illustrate a number of practical advantages resulting from the presence of the mild steel insert. The heat extraction resulting from the insert achieved a rapid rate of cooling in excess of 100°C per minute, producing a high volume fraction of extremely fine M_7C_3 primary carbides. Also, while the fracture toughness of the alloy is more than adequate for the application, the steel insert was found to eliminate shattering of the alloy under inadvertent severe impact loading. The inserts were readily able to be drilled and tapped at its ends, to facilitate mounting of the blow bars. Also, the insert enabled otherwise critical pouring temperature control to be relaxed, to just in excess of 50°C above the liquidus temperature for the alloy, without detriment to the properties of the alloy.

Blow bars prepared in accordance with this Example except for omission of the inserts, and a corresponding increase in alloy volume poured, were found to be unsatisfactory. In



contrast to the Example, those blow bars had a comparable volume fraction of M_7C_3 primary carbides, but with a mean diameter substantially in excess of 75μ , typically about 100μ ; while there was a reduction in fracture toughness of at least about 20%. Performance of those bars was quite inferior to those of the Example, principally in terms of their tendency to spall under in-service impact conditions, and to fail catastrophically under extreme impact load; while they also were found to consistently crack during casting.

10 The following further Examples detail alloys cast to produce iron ore girzzly bars, coal pulverizers, slurry spray nozzles, bone pulverizers, ore chute liners, crusher liner plates and hammer mill components.

EXAMPLE III

Composition - chromium	33.2%
carbon	4.1%
boron	0.74%
manganese	0.50%

Solidification temperature range: $1400^{\circ}\text{C} - 1225^{\circ}\text{C}$

20 Microstructure: primary M_7C_3 carbide

volume fraction	52%
mean diameter	60 microns
Matrix hardness - as cast	780 HV
heat treated	890 HV
Abrasion wear resistance	31.7 mgm
Fracture toughness (K_{IC})	$20 \text{ MNm}^{-3/2}$
Bend tensile strength	600 MPa



EXAMPLE IV

Composition - chromium	26.0%
carbon	4.5%
manganese	0.9%

Solidification temperature range: 1340°C - 1235°C

Microstructure: primary M_7C_3 carbide

volume fraction	29%
mean diameter	50 microns

Matrix hardness - as cast	670 HV
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10 heat treated	750 HV
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Abrasion wear resistance	37.4 mgm
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Fracture toughness (K_{IC})	28 $MNm^{-3/2}$
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Bend tensile strength	850 MPa
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EXAMPLE V

Composition - chromium	35.1%
carbon	4.66%
titanium	0.63%
manganese	0.50%

Solidification temperature range: 1410°C - 1265°C

20 Microstructure: primary M_7C_3 carbide

volume fraction	34%
mean diameter	40 microns

Matrix hardness - as cast	710 HV
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heat treated	900 HV
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Abrasion wear resistance	31.7 mgm
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Fracture toughness (K_{IC})	27 $MNm^{-3/2}$
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Bend tensile strength	850 MPa
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EXAMPLE VI

Composition - chromium	36.0%
carbon	4.54%
manganese	6.0%
Solidification temperature range: 1425°C - 1250°C	
Microstructure: primary M_7C_3 carbide	
volume fraction	34%
mean diameter	50 microns
Matrix hardness - as cast	630 HV
10 heat treated	850 HV
Abrasion wear resistance	44.2 mgm
Fracture toughness (K_{IC})	30 $MNm^{-3/2}$
Bend tensile strength	750 MPa

EXAMPLE VII

Composition - chromium	38.9%
carbon	5.23%
vanadium	3.6%
manganese	0.4%
Solidification temperature range: 1470°C - 1260°C	
20 Microstructure: primary M_7C_3 carbides	
volume fraction	40%
mean diameter	55 microns
Matrix hardness - as cast	680 HV
heat treated	900 HV
Abrasion wear resistance	27.6 mgm
Fracture toughness (K_{IC})	22 $MNm^{-3/2}$
Bend tensile strength	640 MPa

As made clear by the Examples, the fracture toughness values range from about 20 to about 30 $MNm^{-3/2}$, although higher values are obtainable with the alloy of the invention.

In relation to Example I, it should be noted that at the indicated level for molybdenum, it contributes little to the properties of the alloy other than a slight increase in heat treated hardness due to precipitation of a small quantity of secondary carbides. Molybdenum preferably is present, in the absence of other carbide forming elements, at from 6 to 10 wt.%. .

Example III illustrates the significance of boron, even at the low levels specified. The M_7C_3 volume fraction of the composition can be increased with higher boron contents but, as indicated by the fracture toughness and bend tensile strength values, an increase in manganese level is desirable even at the specified level for boron. An increase in boron to about 1 wt.%, preferably with manganese at from 5 to 10 wt.% or higher, would enable hardness values to be increased to about 1000 HV.

Similar results are obtained in Example V by substituting niobium or tantalum for the titanium, while any of these metals can be present to about 5 wt.% to increase the M_7C_3 carbide volume fraction and as cast and heat treated hardnesses. In Example VI, nickel can be substituted for manganese, with some increase in carbide volume fraction and a progressive increase in heat treated hardness for manganese to 13 wt.% and nickel to 10 wt.%.

In Example VII, vanadium can be substituted by molybdenum or tungsten. Also, there can, with advantage in terms of M_7C_3 volume fraction and as cast and heat treated hardnesses, be up to 10 wt.% of those three metals overall without need for increase in manganese content.

In Examples III to VII, the melt was poured as close as practical to the liquidus temperature. In Examples I to VII, the as cast matrix was predominantly austenite with



eutectic carbides, with a small amount of martensite. The matrix also included some secondary carbide precipitated on cooling from 1000°C to 750°C.



The claims defining the invention are as follows:-

1. A tough, abrasion resistant ferrous alloy comprising a cast hypereutectic white iron having in excess of 4.0 wt.% carbon, from 25 to 45 wt.% chromium and:

0 - 15 wt.% manganese,

0 - 10 wt.% molybdenum,

0 - 10 wt.% nickel,

0 - 2 wt.% boron,

0 - 5 wt.% of at least one carbon forming element

10 selected from titanium, tungsten, tantalum, vanadium and niobium, the balance apart from incidental impurities being iron; the total of said at least one carbide forming element being not more than 15 wt.%; the alloy as cast having a minimum thickness dimension of at least 10 mm, and a microstructure comprising a volume fraction in excess of 20% primary carbides of acicular M_7C_3 type and a matrix of eutectic composition; the primary carbides of the M_7C_3 type substantially throughout the alloy having a mean cross-sectional dimension of not more than 75 μ .

2. A ferrous alloy as defined in claim 1, wherein there
20 are at least two of said carbide forming elements to a total of at least 10 wt.%, and at least 5 wt.% manganese.

3. A ferrous alloy as defined in claim 1 or claim 2, wherein there is at least one of manganese and nickel present at a respective level of not less than 2 wt.% and 4 wt.%.

4. A ferrous alloy as defined in any one of claims 1 to 3, wherein there is from 1 to 2 wt.% boron and at least 5 wt.% manganese.

5. A ferrous alloy as defined in any one of claims 1 to 4, wherein there is from 1 to 2 wt.% boron and at least 5 wt.%
3 manganese.



6. A ferrous alloy as defined in claim 1, wherein said matrix is characterized by eutectic carbides and a mixture of austenite and martensite, plus secondary carbides.

7. A ferrous alloy as defined in claim 6, wherein there is from 40 to 60% of one of austenite and martensite relative to the other.

8. A ferrous alloy as defined in claim 1, wherein said matrix is characterized by eutectic carbides, austenite and secondary carbides substantially in the absence of martensite.

10 9. A ferrous alloy as defined in any one of claims 1 to 8, wherein carbon is present at from 4.0 to 7.5 wt.%.

10. A ferrous alloy as defined in claim 9, wherein carbon is present at from 4.5 to 5.5 wt.%.

11. A ferrous alloy as defined in any one of claims 1 to 10, wherein chromium is present at a level of at least 30 wt.%.

12. A ferrous alloy as defined in claim 11, wherein chromium is present at from 30 to 40 wt.%.

13. A ferrous alloy as defined in any one of claims 1 to 12, wherein there is from 1 to 5 wt.% of at least one of titanium, tungsten, tantalum, vanadium and niobium to a total not in excess of 15 wt.% and added as fine particulate carbide to the melt from which said alloy is cast.

14. A ferrous alloy as defined in any one of claims 1 to 13, wherein there is up to 2 wt.% boron added as fine particulate boron carbide to the melt from which the alloy is cast.

15. A ferrous alloy as defined in any one of claims 1 to 14, wherein there is from 1 to 10 wt.% molybdenum added as fine particulate molybdenum carbide to the melt from which the alloy is cast.

30 16. A ferrous alloy as defined in any one of claims 1 to 15,



wherein said volume fraction of primary carbides is from 30 to 60%.

17. A ferrous alloy as defined in any one of claims 1 to 16, wherein said volume fraction is from 40 to 75%.

18. A ferrous alloy as defined in any one of claims 1 to 16, wherein said volume fraction is from 30 to 80%.

19. A ferrous alloy as defined in claim 18, wherein said volume fraction is from 55 to 80%.

20. A ferrous alloy as defined in any one of claims 1 to 19, wherein said M_7C_3 primary carbides have a mean cross-sectional dimension of less than 60 microns.

21. A ferrous alloy as defined in claim 20, wherein said M_7C_3 primary carbides have a mean cross-sectional dimension of less than 50 microns.

22. A ferrous alloy as defined in any one of claims 1 to 21, wherein said alloy is subjected to a heat treatment.

23. A ferrous alloy as defined in claim 22, wherein said heat treatment comprises heating said alloy to a temperature of 750 to 1000°C; followed by furnace or air cooling.

24. A ferrous alloy as defined in claim 23, wherein said heat treatment is at a temperature of about 900°C for 2 to 3 hours.

25. A composite article comprising a metal substrate having metallurgically bonded thereto an alloy as defined in any one of claims 1 to 24.

26. An article as defined in claim 25, wherein said substrate is relative ductiel and said alloy is bonded thereby by being cast against said substrate.

27. An article as defined in claim 26, wherein said substrate is cast within said alloy.



28. An article as defined in claim 25, wherein said substrate is relatively ductile and said alloy is precast and bonded to said substrate by vacuum brazing.

29. An article as defined in any one of claims 26 to 28, wherein a filler metal is applied to said substrate prior to said alloy being bonded thereto.

30. An article as defined in claim 29, wherein said filler metal is copper.

10 31. An article as defined in any one of claims 25 to 30, wherein said substrate has a weight of at least 10% of said article.

32. A method of forming a tough, abrasion resistant ferrous alloy, comprising casting a melt of a ferrous alloy according to any one of claims 1 to 24, wherein said melt is poured at a temperature not less than 20°C above the liquidus temperature for the alloy and not more than 100°C above that liquidus temperature, and is cast to a volume having a minimum thickness dimension of at least 10 mm.

20 33. A method as defined in claim 32, wherein said melt is poured at a temperature not more than 40°C above said liquidus temperature.

34. A method according to claim 32, wherein said melt is poured at a temperature not more than 20°C above said liquidus temperature.

35. A method as defined in claim 32, wherein said melt is poured at a temperature substantially at said liquidus temperature and, in any event, not more than 5°C above said liquidus temperature.

36. A method as defined in any one of claims 32 to 35, wherein said melt is cooled down to the solidus temperature for

the alloy at a rate of at least 50°C per minute.

37. A method as defined in claim 36, wherein said melt is cooled down to the said solidus temperature at a rate of at least 100°C per minute.

38. A method as defined in any one of claims 32 to 37, wherein said melt is cast against a metal substrate so that the alloy, on solidification, is metallurgically bonded to said substrate to provide a composite article.

39. A method as defined in claim 38, wherein said alloy is cast to a volume such that the substrate comprises at least 10% by weight of said article.

40. A method as defined in any one of claims 32 to 37, wherein said alloy when cast is applied to a substrate and metallurgically bonded thereto by vacuum brazing to provide a composite article.

INTERNATIONAL SEARCH REPORT

International Application No PCT/AU 84/00096

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC Int. Cl. ³ C22C 37/06, C22C 37/08, 33/08, C21C 1/08, C21D 1/18, 1/613, 1/84, 5/04, 9/00; B22D 19/02, 19/04, 19/16, 15/00, B23K 1/04, 1/19.		
II. FIELDS SEARCHED B32B 15/01, 15/18, B02C 17/22, 23/00.		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
IPC	C22C 37/06, 37/08, C21C 1/08	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁵		
AU: IPC as above; Australian Classification 15.8		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category [*]	Citation of Document, ¹⁵ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
X	AU, B, 4422/66 (424202) (EUTECTIC WELDING ALLOYS CORP) 19 October 1967 (19.10.67)	(1,3,4,9-15, 22,25,26)
X	AU, B, 27601/67 (433699) (EUTECTIC WELDING ALLOYS CORP) 27 March 1969 (27.03.69)	(1,3,9-15, 25,26)
X	AU, B, 43163/72 (470081) (MICHEL FELTZ) 13 December 1973 (13.12.73)	(1,9,10,12, 13,15,20-22)
X,P	AU, A, 22760/83 (VICKERS AUSTRALIA LIMITED) 22 March 1984 (22.03.84)	(25-31)
X	FR, A, 2036160 (ZAVOD SELSKOKHOZYAISTVENNOGO MACHINOSTROENIYA IM. OKTYABRSKOI RESOLUTSII) 24 December 1970 (24.12.70)	(1,9-12)
X	JP, A, 54-149012 (KOGYO GIJUTSIN), 21 November 1979 (21.11.79) JAPATIC English Language Abstract)	(1,25,26)
(continued)		
<p>[*] Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ¹	Date of Mailing of this International Search Report ²	
3 September 1984 (03.09.84)	(06-09-84) 6, SEPTEMBER 1984	
International Searching Authority ¹	Signature of Authorized Officer ²⁰	
Australian Patent Office	H.W. NESS <i>H.W. Ness</i>	

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

- | | | |
|---|---|--------------------|
| X | Metals technology, Volume 6 Part 11, issued 1979 November (Metals Society, London), I.R. Sare, Abrasion Resistance and Fracture Toughness of White Cast Irons, see pages 412 to 419. | (1,6-12, 16-23,25) |
| X | Australian Welding Journal, Volume 22, No.1, issued 1978 January/February (Associated Business Publications, Sydney), C. M. Perrott and I. R. Sare, 'Abrasion Testing of Hard-facing Alloys,' see pages 4 to 8. | (1,9-12,22) |

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹⁰

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers because they relate to subject matter ¹² not required to be searched by this Authority, namely:
2. ☐ Claim numbers because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹³, specifically:

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ¹¹

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON
INTERNATIONAL APPLICATION NO. PCT/AU 84/00096

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document
Cited in Search
Report

Patent Family Members

AU 27601/67	BE 703933	CH 490139	DE 1558880
	GB 1205793	GB 1206378	GB 1206379
	GB 1206380	NL 6712873	US 3428442

AU 43163/72	BR 7204244	CA 990105	DE 2230864
	GB 1390011	IT 959133	LU 63431
	US 3834950	ZA 723826	

END OF ANNEX